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Calorimetric and Computational Study of Thiacyclohexane 1-Oxide and Thiacyclohexane 1,1-Dioxide (Thiane Sulfoxide and Thiane Sulfone). Enthalpies of Formation and the Energy of the S═O Bond

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A rotating-bomb combustion calorimeter specifically designed for the study of sulfur-containing compounds [*J. Chem. Thermodyn.* **1999**, *31*, 635] has been used for the determination of the enthalpy of formation of thiane sulfone, **4**, $\Delta_f H^\circ_m(g) = -394.8 \pm 1.5$ kJ mol^{-1}. This value stands in stark contrast with the enthalpy of formation reported for thiane itself, $\Delta_f H^\circ_m(g) = -63.5 \pm 1.0$ kJ mol^{-1}, and gives evidence of the increased electronegativity of the sulfur atom in the sulfonyl group, which leads to significantly stronger C−SO$_2$ bonds. Given the known enthalpy of formation of atomic oxygen in the gas phase, $\Delta_f H^\circ_m(O,g) = +249.18$ kJ mol^{-1}, and the reported bond dissociation energy for the S═O bond in alkyl sulfones, BDE(S═O) = +470.0 kJ mol^{-1}, it was possible to estimate the enthalpy of formation of thiane sulfoxide, **5**, a hygroscopic compound not easy to use in experimental calorimetric measurements, $\Delta_f H^\circ_m(\mathbf{5}) = -174.0$ kJ mol^{-1}. The experimental enthalpy of formation of both **4** and **5** were closely reproduced by theoretical calculations at the G2(MP2)+ level, $\Delta_f H^\circ_m(\mathbf{4}) = -395.0$ kJ mol^{-1} and $\Delta_f H^\circ_m(\mathbf{5}) = -178.0$ kJ mol^{-1}. Finally, calculated G2(MP2)+ values for the bond dissociation energy of the S═O bond in cyclic sulfoxide **5** and sulfone **4** are +363.7 and +466.2 kJ mol^{-1}, respectively.

Introduction

Over the past few years, we have been involved in the systematic quantitative comparison of thermodynamic data, particularly the standard enthalpies of formation, of six-membered sulfur-containing heterocycles.[1−3] Consideration of the corresponding data for the oxygen analogues is frequently essential for a proper rationalization of the thermochemical results. For example, relative to cyclohexane, **1**, the enthalpy of formation of oxane, **2**, is much more negative, −123.3 and −223.4 kJ mol^{-1}, respectively (Figure 1). By contrast, the enthalpy of formation of thiane, **3**, is −63.5 kJ mol^{-1}, less negative than that for cyclohexane. As discussed by Wiberg and co-workers,[4] the lower electronegativity of sulfur relative to oxygen results in diminished Coulombic attraction between the heteroatom and bonded carbon atoms, and thus weaker C−S bonds.

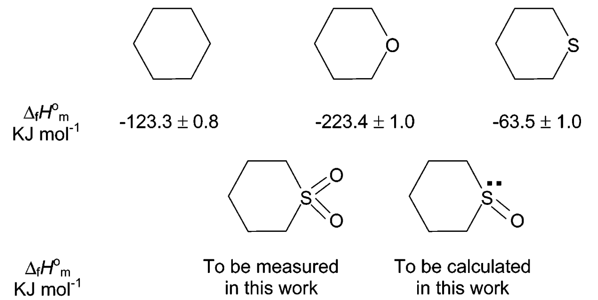

FIGURE 1. Comparison of the experimental gas-phase enthalpies of formation of cyclohexane, oxane, and thiane.

Over the past three or four decades the use of sulfones in organic synthesis has increased enormously, and now rivals applications of the carbonyl functionality in areas such as carbon−carbon bond formation[5] (Scheme 1).

The growing relevance of the sulfone group motivated the present study; in particular, we aimed at the deter-

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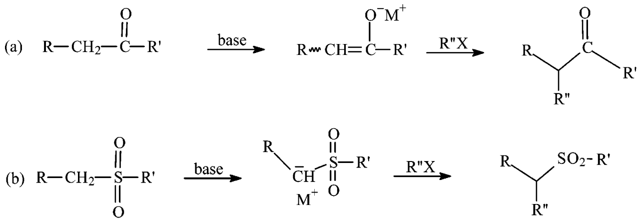
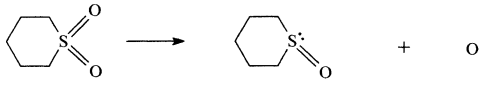
SCHEME 1



mination of the enthalpy of formation of thiane sulfone (thiacyclohexane 1,1-dioxide, tetrahydro-2*H*-thiopyran 1,1-dioxide, pentamethylene sulfone, **4**) (Figure 1). Indeed, thermochemical data on sulfone **4** should be useful to gain [by comparison with $\Delta_f H°_m(\mathbf{1})$, $\Delta_f H°_m(\mathbf{2})$, and $\Delta_f H°_m(\mathbf{3})$; Figure 1 and ref 6] relevant information on $C-SO_2$ and S=O bond strengths. In this regard, $C-SO_2$ bonds in alkyl sulfones are generally shorter than C−S bonds in analogous sulfides (1.77 vs 1.81 Å, on average[7]), suggesting stronger bonding in the former. Furthermore, it is generally accepted that 3*d* orbitals in sulfur strengthen the S=O bond via $d_\pi - p_\pi$ back-bonding.[8]

Thermochemical studies of sulfone derivatives are mostly limited to those of Busfield and Mackle and their co-workers in the 1960s.[9,10] Most relevant, from the collected thermochemical data, the bond dissociation energy (BDE) for the S=O bond in alkyl sulfones was estimated[10] as BDE = +470 kJ mol^{-1}. This datum is of great importance in the present work because, taken together with the known[11] enthalpy of formation of atomic oxygen in the gas phase, $\Delta_f H°_m(\mathrm{O,g}) = +249.18$ kJ mol^{-1}, it should allow for the calculation of the enthalpy of formation in the gas phase of sulfoxide **5** (thiacyclohexane 1-oxide, tetrahydro-2*H*-thiopyran 1-oxide, pentamethylene sulfoxide), a hygroscopic compound not easy to use in experimental calorimetric measurements (eq 1).



4 **5** (1)

Changing the number of oxygens attached to sulfur in sulfones and sulfoxides causes considerable differences in the physicochemical properties of these compounds.[12] In both kinds of compounds sulfur is hypervalent; i.e., it is surrounded by more than the eight electrons normally associated with completely filled *s* and *p* shells, and participation of 3*d* orbitals is required to make up the S−O bonding.[13] While there is agreement in describing the S−O bonds of sulfones as double bonds and $-SO_2-$ as a rather "rigid" fragment,[7,14] the nature of bonding in sulfoxides is controversial. Most likely, the best representation of the sulfinyl moiety is a hybrid of the semipolar single-bond (S^+-O^-) and double-bond (S=O) forms.[15]

Results and Discussion

Experimental Enthalpies of Formation. The results of combustion experiments for **4** are given in Table 1 and correspond to the reaction

$$C_5H_{10}O_2S(c) + 8O_2 + 111H_2O(l) \rightleftarrows 5CO_2 + [H_2SO_4{\cdot}115H_2O](l) \quad (2)$$

The symbols in this table have the same meaning as in ref 16, and the experimental values have been derived as in ref 17. The uncertainties of the standard molar energy and enthalpy of combustion are twice the final overall standard deviation of the mean and were estimated as outlined by Olofsson.[18]

To derive $\Delta_f H°_m(\mathrm{cr})$ from $\Delta_c H°_m(\mathrm{cr})$, the standard molar enthalpies of formation of $H_2O(l)$ and $CO_2(g)$, at T = 298.15 K, respectively, −285.839 ± 0.042 and −393.51 ± 0.13 kJ mol^{-1}, were used.[19]

Vapor pressures were determined at different temperatures in the interval 299.87−314.83 K, and the results are given in Table 2.

The Clausius−Clapeyron equation fitted to the results of pressure and temperature by the least-squares method is $\ln p = -(10571 \pm 32)T^{-1} + (33.1 \pm 0.1)$. The molar enthalpy of sublimation corresponding to the mean temperature $\langle T_m \rangle = 307.35$ K of its experimental range is $\Delta_{sub}H°_m = 87.9 \pm 0.3$ kJ mol^{-1}. The enthalpy of sublimation determined at $\langle T_m \rangle$ was adjusted at T = 298.15 K by means of eq 3 according to that described in

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TABLE 1. Results of Combustion Experiments of Thiacyclohexane 1,1-Dioxide at $T = 298.15$ K

m'(compd)/g	1.02026	1.07757	1.16571	1.17606	1.17957
m''(polyethene)/g	0.07312	0.07896	0.07491	0.07850	0.07575
m'''(vaseline)/g	0.09077	0.00000	0.00000	0.00000	0.00000
m''''(fuse)/g	0.00232	0.00222	0.00231	0.00228	0.00228
$\Delta T_c/\mathrm{K} = (T_f - T_i + \Delta T_{corr})/\mathrm{K}$	−1.1887	−1.1037	−1.1778	−1.1924	−1.1918
ϵ(calor) $(-\Delta T_c)$/kJ	−34.3175	−31.8649	−34.0033	−34.4263	−34.4087
ϵ(cont) $(-\Delta T_c)$/kJ	−0.0600	−0.0552	−0.0593	−0.0602	−0.0601
ΔU_{ign}/kJ	0.0004	0.0004	0.0004	0.0004	0.0004
$\Delta U_{dec}(HNO_3)$/kJ	0.0587	0.0436	0.0598	0.0390	0.0564
$\Delta U_{diln}(H_2SO_4)$/kJ	−0.00316	−0.00377	−0.00469	−0.00479	−0.00483
ΔU(corr to std states)/kJ	0.0252	0.0230	0.0241	0.0247	0.0245
$-m''\Delta_c u°$(polyethene)/kJ	3.3909	3.6613	3.4735	3.6400	3.5124
$-m'''\Delta_c u°$(vaseline)/kJ	4.1834	0.0000	0.0000	0.0000	0.0000
$-m''''\Delta_c u°$(fuse)/kJ	0.0405	0.0386	0.0403	0.0397	0.0398
$\Delta_c u°$(compound)/kJ g^{-1}	−26.1521	−26.1304	−26.1381	−26.1448	−26.1454
$\langle\Delta_c u°(298.15\ \mathrm{K})\rangle$/kJ g^{-1}			−26.1422 ± 0.0037		

TABLE 2. Vapor Pressures of Thiacyclohexane 1,1-Dioxide

T/K	t^a/s	Δm^b/mg	p^c/Pa	$10^2(\delta p/p)^d$
299.87	21600	2.57	0.119	0.293
303.03	23460	3.97	0.171	−0.253
305.84	15000	3.50	0.237	0.300
308.86	26580	8.72	0.334	0.773
311.92	14160	6.40	0.463	−0.178
314.83	12000	7.39	0.634	−0.105

[a] Time for the experiment. [b] Mass of the sublimed substance. [c] Vapor pressure. [d] $\delta p/p$ denotes the deviation of the experimental vapor pressures from the values computed using eq 19.

ref 20a. The term $C_{p,\mathrm{m}}$ is the heat capacity of the solid phase and was estimated according to a group additivity approach.[20b]

$$\Delta^{g}_{cr}H_m°(298.15\ \mathrm{K}) = \Delta^{g}_{cr}H_m°(\langle T_m\rangle/\mathrm{K}) + \{0.75\ \mathrm{J\ K^{-1}\ mol^{-1}} + 0.15C_{p,m}\}\{\langle T_m\rangle - 298.15\ \mathrm{K}\} \quad (3)$$

Table 3 gives the standard molar energy and enthalpy of combustion and formation of thiacyclohexane 1,1-dioxide, in the crystalline state at $T = 298.15$ K, and the standard molar enthalpy of sublimation and the standard molar enthalpy of formation in the gas state.

Neither combustion nor sublimation enthalpies of this compound were found for comparison with our results.

Considering reaction 1, with the experimental value of the enthalpy of formation in the gas state of **4** at hand, and given the known enthalpy of formation of atomic oxygen in the gas phase, $\Delta_f H°_m(\mathrm{O,g}) = +249.18$ kJ mol^{-1},[11] as well as the reported bond dissociation energy for the S═O bond in alkyl sulfones,[10] BDE(S═O) = +470.0 kJ mol^{-1}, it was possible to estimate the enthalpy of formation of **5**, $\Delta_f H°_m$ (**5**) = −174.0 kJ mol^{-1}.

Molecular and Electronic Structures. Geometries of **5** and **4**, both experimental[21,22] and optimized at the MP2(FULL)/6-31G(3df,2p) level of theory, are presented in Table 4.

In both compounds, the most stable form is the chair conformation, belonging to the symmetry point group C_s (see Figure 2). The chair structure is similar to that of cyclohexane but is more puckered to accommodate the bond angles and bond lengths characteristic of sulfur. In thiacyclohexane 1-oxide, the oxygen atom can be in the axial or equatorial position. Calculations show that the axial position is preferred, according to all previous experimental and theoretical studies.[23−32] At the MP2(FULL)/6-31G(d) level of theory, the structure with the O atom in the equatorial position is 7.4 kJ mol^{-1} higher in energy. There is a range of experimental conformational free energy values from −0.8 to −5.4 kJ mol^{-1}, since $-\Delta G°$ is strongly solvent dependent[28] and is influenced by the presence of monomer and dimer forms.[25,26c] It has been suggested[26c] that the $-\Delta G° = -5.4$ kJ mol^{-1} is the correct value for thiacyclohexane 1-oxide in the gas phase or under experimental conditions of high dilution. An early interpretation[23] attributed the axial preference of the sulfoxide oxygen to an attractive interaction between the oxygen and the syn-axial hydrogens, but later molecular mechanics calculations[26b] did not support that idea.

The boat and twist conformers are also minima of the potential energy surface of the molecules studied, but calculations at the HF/6-31G(d) level indicate that they are 27.8 and 23.3 kJ mol^{-1} higher in energy, respectively, than the chair conformer in the case of thiacyclohexane 1,1-dioxide and in the range 27.0−33.5 kJ mol^{-1} higher in energy than the chair conformer in the case of thiacyclohexane 1-oxide (because of the lower symmetry, there are three twist and four boat conformers).

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TABLE 3. **Thiacyclohexane 1,1-Dioxide: Standard Molar Energy of Combustion, $\Delta_c U^\circ_m$, and Enthalpies of Combustion, $\Delta_c H^\circ_m$, Formation of the Solid, $\Delta_f H^\circ_m$, Sublimation, $\Delta_{sub} H^\circ_m$, and Sublimation of the Gas, $\Delta_f H^\circ_m$, at $T = 298.15$ K and $p^\circ = 101.325$ kPa**

$\Delta_c U^\circ_m$(cr)/kJ mol^{-1}	$\Delta_c H^\circ_m$(cr)/kJ mol^{-1}	$\Delta_f H^\circ_m$(cr)/kJ mol^{-1}	$\Delta_{sub} H^\circ_m$/kJ mol^{-1}	$\Delta_f H^\circ_m$(g)/kJ mol^{-1}
−3508.3 ± 1.3	−3515.7 ± 1.3	−483.0 ± 1.4	88.2 ± 0.3	−394.8 ± 1.4

TABLE 4. **Calculated and Experimental Structures of Thiacyclohexane 1-Oxide and Thiacyclohexane 1,1-Dioxide**[a]

	thiacyclohexane 1-oxide		thiacyclohexane 1,1-dioxide	
	calcd[b]	exptl[c]	calcd[b]	exptl[d]
S−O$_{ax}$	1.487	1.483	1.437	1.439
S−O$_{eq}$			1.441	1.447
S−C	1.798	1.816	1.762	1.758
(S)C−C	1.515	1.538	1.519	1.526
(C)C−C(C)	1.518	1.539	1.520	1.521
OSO			120.5	116.9
CSO$_{ax}$	106.3	108.1	107.5	109.0
CSO$_{eq}$			109.5	109.5
CSC	94.9	91.1	100.6	102.3
CCS	111.4	112.5	110.5	111.0
(S)CCC	111.8	111.5	111.8	112.5
(C)CCC(C)	111.5	114.8	112.4	113.7
Θ[e]	108.8	109.0	109.6	110.5
Φ[f]	61.6	61.1	59.7	57.4

[a] Bond lengths in angstroms and bond angles in degrees. [b] Geometry optimized at the MP2(FULL)/6-31G(3df,2p) level of theory. [c] Gas-phase electron diffraction data taken from ref 21. [d] X-ray crystal data taken from ref 22. [e] Mean bond angle in the ring. [f] Mean torsional angle in the ring.

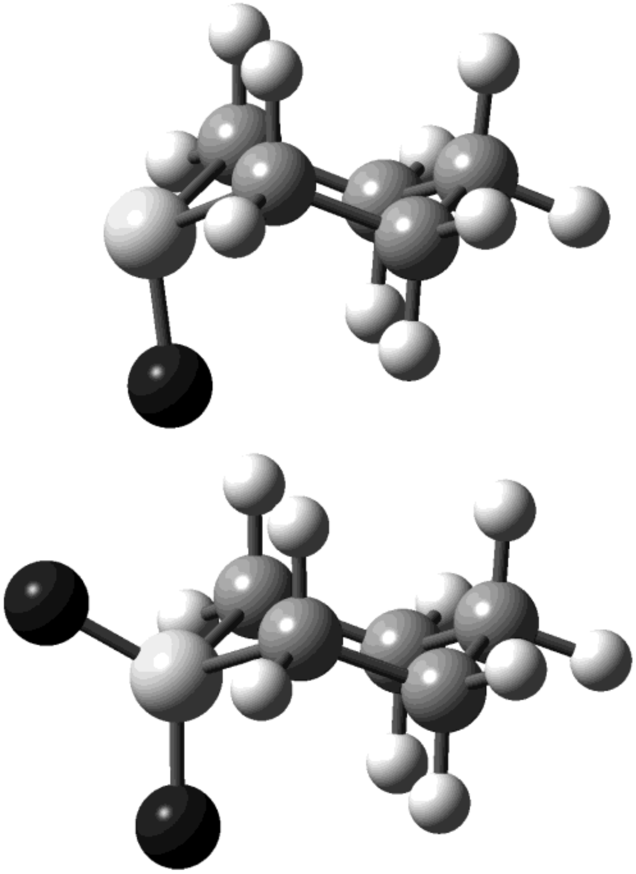

FIGURE 2. Chair conformations (C_s) of thiacyclohexane 1-oxide and thiacyclohexane 1,1-dioxide, optimized at the MP2-(FULL)/6-31G(3df,2p) level.

The calculated structural parameters are in very good agreement with the experimental ones. For both sulfoxides and sulfones, the length of the S═O bond is the most important structural parameter. The agreement between calculated and experimental S═O bond distances is excellent. It is interesting to note that, in thiacyclohexane 1,1-dioxide, the S−O$_{ax}$ distance is slightly shorter than the S−O$_{eq}$ distance.

The bond configuration of all sulfoxides is characterized by a pyramidal arrangement. In terms of the valence shell electron pair repulsion (VSEPR) theory,[33] it is an AX$_3$E structure with three ligands and one lone pair of electrons around the central sulfur atom. It is a general observation[34] that in sulfoxides the XSX angle is smaller than the XSO angle. This fact is observed in thiacyclohexane 1-oxide (see Table 4). This result is fully consistent with VSEPR predictions, according to which an angle involving multiple bonds will be greater than an angle involving single bonds only. The sulfonyl group, in addition, has the bond angle OSO and the corresponding O···O nonbonded distance as important structural parameters. According to the VSEPR predictions cited above, the relationship among the sulfur bond angles should be OSO > XSO > XSX, as is observed in thiacyclohexane 1,1-dioxide (see Table 4). It has been observed[34] that the nonbonded O···O distance remains practically constant in a relatively large series of sulfonyl derivatives, 2.484 Å being the experimental mean value. The calculated value for thiacyclohexane 1,1-dioxide is 2.56 Å. It was suggested[35] that this result indicates that the nonbonded oxygen−oxygen interactions may be as important in determining the geometry of the sulfone group as the bonded interactions considered in the VSEPR model. It was further suggested[33] that the emerging pattern of results can be visualized by a tetrahedral arrangement of the XSO$_2$Y group with the sulfur atom in the center of the tetrahedron and the two oxygen atoms at two of the apexes. As the two ligands are changed, the two oxygen atoms remain in their position, while the sulfur atom may move up and down along the vector corresponding to the bisector of the OSO angle.[33]

If we compare the experimental geometries of the compounds studied with that of thiane,[36] it is interesting to note that the C−S bond lengths are very similar in thiane and thiacyclohexane 1-oxide (1.811 and 1.816 Å, respectively) but significantly shorter in thiacyclohexane

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1,1-dioxide (1.758 Å), whereas the C−C bond lengths are very similar in the three compounds. The CSC angle is larger in thiacyclohexane 1,1-dioxide (102.3°) than in thiane (97.6°) or in thiacyclohexane 1-oxide (91.1°). This behavior has been observed in other compounds. The bond angle XSX always decreases in going from a sulfone to the analogous sulfoxide, whereas from sulfoxide to sulfide there is an increase in the value.[34] This fact is in apparent disagreement with VSEPR considerations; it would have been expected that the XSX angle should further decrease in the analogous sulfides. An explanation[34] for this apparent anomaly may be that, for a general applicability of VSEPR considerations,[37] not only the bond angle variations but also the angles of the lone pairs must be considered. The situation is especially complicated in the case of sulfides, where three kinds of interactions are present: bond/bond, bond/lone pair, and lone pair/lone pair.

We have also obtained the distances between the oxygen atoms and the syn-axial hydrogens. This distance is significantly shorter in the case of thiacyclohexane 1-oxide (2.58 Å) than in the case of the axial oxygen in thiacyclohexane 1,1-dioxide (2.71 Å). This seems to confirm the idea of Johnson and McCants,[23] attributing the axial preference of the sulfoxide oxygen to an attractive interaction between the oxygen and the syn-axial hydrogens.

It has been observed[35,38] that the introduction of a sulfur heteroatom into a six-membered carbon ring increases the ring puckering in comparison with the conformation of cyclohexane.

The relation between torsional angles, φ, and valency angles, θ, in a chair form cyclohexane ring is given by

$$\cos \varphi = -(\cos \theta)/[1 + \cos \theta] \qquad (4)$$

This relation, which holds exactly for cyclohexane,[39] can be used also for deformed chair forms of lower symmetry six-membered rings[40] provided that the individual angles φ and θ are replaced by the averages of the six torsional angles, Φ, and the six valency angles, Θ:

$$\cos \Phi = -(\cos \Theta)/[1 + \cos \Theta] \qquad (5)$$

The average torsional angle, Φ, which is determined by a delicate balance among valency, torsional, and nonbonded forces, is therefore an easily calculated and convenient index of the puckering in six-membered rings. Calculated and experimental values of Θ and Φ mean angles for both compounds studied are collected in Table 4.

The Φ torsional angle of thiacyclohexane 1,1-dioxide has a value similar to that obtained for thiane ($\Phi = 58.2$, calculated[3] from experimental angles), indicating that both rings are similarly puckered. However, the most puckered ring is that of thiacyclohexane 1-oxide, with a Φ angle similar to that obtained for 1,3-dithiane ($\Phi = 60.9$).[3]

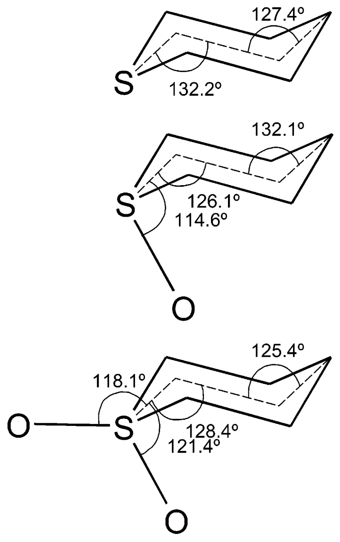

FIGURE 3. Angles between planes in thiacyclohexane 1-oxide and thiacyclohexane 1,1-dioxide, calculated at the MP2(FULL)/6-31G(3df,2p) level.

We have also calculated the angles between planes in the compounds studied and compared with the values calculated for thiane.[3] The corresponding values are shown in Figure 3. The angles in thiane are larger than in thiacyclohexane 1,1-dioxide, confirming that the structure of thiacyclohexane 1,1-dioxide is more puckered. It is interesting to note that the angle between the $S-O_{ax}$ bond and the CSC plane is significantly smaller in the sulfoxide (114.6°) than in the sulfone (121.4°), confirming the attractive interactions between the axial oxygen atom and the syn-axial hydrogens.

To our knowledge, the infrared or Raman spectra of thiacyclohexane 1,1-dioxide had not been previously reported, and only the infrared spectrum of thiacyclohexane 1-oxide is known.[41] The computed vibrational frequencies at the MP2(FULL)/6-31G(d) level, scaled by the factor 0.9427 recommended by Scott and Radom,[42] are collected in Table S4 of the Supporting Information for the two compounds studied. An assignation of the frequencies to the different normal vibrational modes of the molecules has been made comparing the computed vibrations with the assignments of Hase and Kawano.[41]

The comparison between the experimental and calculated frequencies for thiacyclohexane 1-oxide is very good. The only discrepancies are in the assignment of the S=O wagging and one of the skeletal deformations (see Table S4). Not taking into account these two frequencies, the correlation equation between calculated and experimental frequencies is

$$\nu(\text{calcd}) = -(19.5 \pm 5.3) + (1.0212 \pm 0.0032)\nu(\text{exptl}) \qquad (6)$$

in inverse centimeters; $n = 43$; $R = 0.9998$; $\text{sd} = 18.3\ \text{cm}^{-1}$

A comparison between the fundamental frequencies calculated for both compounds studied can be made. The

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most important difference occurs in the S═O stretching modes. In the sulfoxide there is only one, at 1036.0 cm^{-1}, whereas in the sulfone there are two, the S═O symmetric stretching vibration, at 1098.5 cm^{-1}, and the asymmetric one, at 1276.7 cm^{-1}. The calculated $\nu_{S=O}$ frequency in thiacyclohexane 1-oxide (1036.0 cm^{-1}) is typical of the axial form. It is already known[43] that the S═O stretching frequency of the axial form is lower than that of the equatorial form.

The other differences are in the S═O rocking and wagging vibrations. In thiacyclohexane 1-oxide $\rho_{S=O}$ is assigned to the vibration at 301.1 cm^{-1} and $\omega_{S=O}$ to the vibration at 415.0 cm^{-1}, whereas in thiacyclohexane 1,1-dioxide there are two $\rho_{S=O}$ vibrations, at 254.6 and 374.7 cm^{-1}, and another two $\omega_{S=O}$ vibrations that appear at 413.7 and 463.7 cm^{-1}. One of the ν_{C-S} and ν_{C-C} vibrational modes is also affected by the presence of one or two oxygen atoms in the molecule, but all the other vibrational modes appear at very similar frequencies in both compounds studied: the ten CH_2 stretching modes (2906−3009 cm^{-1}), the five CH_2 scissoring deformations (1417−1469 cm^{-1}), the five CH_2 wagging deformations (1276−1357 cm^{-1}), the five CH_2 twisting modes (1078−1248 cm^{-1}), and the five CH_2 rocking modes (776−999 cm^{-1}). The skeletal deformations are all expected in the frequency region below 535 cm^{-1}.

An important characteristic of the ground electronic state of a molecule is the ionization potential, IP. The first ionization potential for thiacyclohexane 1,1-dioxide has been experimentally determined[44] by means of photoelectron spectroscopy, the value being 10.24 eV. To our knowledge, there is not any experimental determination of the ionization potential for thiacyclohexane 1-oxide.

We have calculated the IP values for the compounds studied according to Koopmans' theorem.[45,46] The IP and the electron affinity, EA, correspond approximately to the negative of the energy of the highest occupied molecular orbital, HOMO, and the lowest unoccupied molecular orbital, LUMO, respectively.

$$\mathrm{IP} = -E_{\mathrm{HOMO}} \qquad \mathrm{EA} = -E_{\mathrm{LUMO}} \tag{7}$$

The calculated IP values for thiacyclohexane 1-oxide and thiacyclohexane 1,1-dioxide are 9.70 and 11.43 eV, respectively, obtained at the MP2(full)/6-31G(3df,2p) level. Electron affinities of −4.98 and −4.86 eV, respectively, have been obtained. The calculated HOMO−LUMO energy gap is larger in thiacyclohexane 1,1-dioxide (16.3 eV) than in thiacyclohexane 1-oxide (14.7 eV). This is a general behavior in sulfones and sulfoxides.[47] A consequence of this is the fact that sulfones are transparent in the UV region, in contrast to sulfoxides.[12] A low HOMO−LUMO gap frequently results in high reactivity,[48] as is the case for the compounds studied.

TABLE 5. G2(MP2)-Calculated Energies, at 0 K, and Enthalpies, at 298 K, for Thiacyclohexane 1-Oxide, Thiacyclohexane 1,1-Dioxide, and the Reference Compounds Used in This Work[a]

	G2(MP2)		G2(MP2)+[b]	
compd	E_0	H_{298}	E_0	H_{298}
5	−668.97473	−668.96670	−668.97390	−668.96588
4	−744.12824	−744.11959	−744.12844	−744.11978
3	−593.85914	−593.85199	−593.85819	−593.85104
dimethyl sulfoxide	−552.47881	−552.47222	−552.47858	−552.47199
dimethyl sulfone	−627.63218	−627.62505	−627.63301	−627.62588
methane	−40.40966	−40.40584	−40.40959	−40.40578
ethane	−79.62893	−79.62445	−79.62878	−79.62429
propane	−118.85309	−118.84751	−118.85281	−118.84723
cyclohexane	−235.34438	−235.33749	−235.34357	−235.33669

[a] All values in hartrees. [b] Values obtained using the G2(MP2) scheme, from geometries optimized at the MP2(FULL)/6-31G(3df,2p) level. See the text.

Theoretical Enthalpies of Formation. G2(MP2)[49] calculated energies, at 0 K, for the compounds studied are given in Table 5.

To calculate enthalpy values at 298 K, the difference between the enthalpy at temperature T and 0 K can be evaluated according to standard thermodynamics.[50] The thermal correction in Gaussian-*n* theories is made using scaled (0.8929) HF/6-31G(d) frequencies for the vibrations in the harmonic approximation for vibrational energy,[51] the classical approximation for translation (3/2 RT) and rotation (3/2 RT for nonlinear molecules, and RT for linear molecules), and an additional RT for converting energy to enthalpy (the pV term). G2(MP2) enthalpies at 298 K for the compounds studied are also collected in Table 5.

In standard Gaussian-*n* theories, theoretical enthalpies of formation are calculated through atomization reactions. We have detailed this method in previous studies.[52] Raghavachari et al.[53] have proposed to use a standard set of isodesmic reactions, the "bond separation reactions",[54] where all formal bonds between non-hydrogen atoms are separated into the simplest parent molecules containing these same kinds of linkages, to derive the theoretical enthalpies of formation. However, this method is not applicable in the case of the compounds studied, because the bond separation isodesmic reactions for thiacyclohexane 1-oxide and thiacyclohexane 1,1-dioxide are reactions 8 and 9, respectively, and the experimental enthalpies of formation of two of the reference compounds, H_2SO and H_2SO_2, are not available.

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$$C_5H_{10}OS(g) + 5CH_4(g) + 2H_2S(g) \rightarrow 4CH_3CH_3(g) + 2CH_3SH(g) + H_2SO(g) \quad (8)$$

$$C_5H_{10}O_2S(g) + 5CH_4(g) + 2H_2S(g) \rightarrow 4CH_3CH_3(g) + 2CH_3SH(g) + H_2SO_2(g) \quad (9)$$

We have used in this work four isodesmic reactions using as references Me_2SO and Me_2SO_2, reactions 10 and 11 in the case of the sulfoxide compound, and reactions 12 an 13

$$C_5H_{10}OS(g) + 5CH_4(g) \rightarrow 4CH_3CH_3(g) + Me_2SO(g) \quad (10)$$

$$C_5H_{10}OS(g) + CH_3CH_2CH_3(g) \rightarrow c\text{-}C_6H_{12}(g) + Me_2SO(g) \quad (11)$$

$$C_5H_{10}O_2S(g) + 5CH_4(g) \rightarrow 4CH_3CH_3(g) + Me_2SO_2(g) \quad (12)$$

$$C_5H_{10}O_2S(g) + CH_3CH_2CH_3(g) \rightarrow c\text{-}C_6H_{12}(g) + Me_2SO_2(g) \quad (13)$$

in the case of the sulfone. The calculated values for the enthalpies of formation of thiacyclohexane 1-oxide and thiacyclohexane 1,1-dioxide, at the G2(MP2) level of theory, using atomization and isodesmic reactions,[55] are shown in Table 6.

A further step in obtaining reliable theoretical values of $\Delta_f H°_m$ for the compounds studied is the consideration of a more sophisticated basis set in the optimization of their geometries. The availability of 3*d* orbitals in sulfur is the main factor responsible for its reactivity behavior, so the adequate description of the geometry and electronic properties of sulfur-containing compounds would require the inclusion of supplementary d functions in the basis set. We have reoptimized the geometries of the compounds studied at the MP2(FULL)/6-31G(3df,2p) level and have also carried out the single-point calculations using a scheme similar to that in the G2(MP2) formalism.[49] This approach will be designed as G2-(MP2)+. The $\Delta_f H°_m$ values for the compounds studied, calculated at this computational level, are collected in Table 6.

As can be seen in that table, the $\Delta_f H°_m$ values for thiacyclohexane 1,1-dioxide, calculated from G2(MP2) and G2(MP2)+ energies, using the atomization reaction scheme are less negative than the experimental value. These calculated values can be modified introducing spin−orbit and bond additivity (BAC) corrections.[56] This procedure has been detailed in a previous study.[3] The modified $\Delta_f H°_m$ values are shown in Table 6. As can be seen, the new values are more negative than the experimental one, indicating that the correction is too high in the case of thiacyclohexane 1,1-dioxide.

When isodesmic reactions 12 and 13 are used to calculate the heat of formation of thiacyclohexane 1,1-dioxide, the values obtained are more negative than the experimental value.

We can also use another type of reaction to calculate the enthalpies of formation of the compounds studied, the S═O bond dissociation reactions, similar to reaction 1:[57]

$$\text{thiacyclohexane 1-oxide} \rightarrow \text{thiane} + O \quad (14)$$

$$\text{thiacyclohexane 1,1-dioxide} \rightarrow \text{thiane} + 2O \quad (15)$$

The calculated S═O bond dissociation enthalpies are 363.3 and 363.7 kJ mol^{-1}, obtained at the G2(MP2) and G2(MP2)+ levels, respectively, for the sulfoxide compound, and 463.5 and 466.2 kJ mol^{-1} for the sulfone. These values are in good agreement with those obtained by Herron[10] from experimental heats of formation of a series of acyclic sulfoxides and sulfones, 373 ± 15 and 470 ± 12 kJ mol^{-1}, respectively.

The enthalpies of formation of both compounds studied obtained using reactions 1, 14, and 15 are collected in Table 6. It has to be noted that the $\Delta_f H°_m$ value calculated for thiacyclohexane 1,1-dioxide using reaction 15 is in very good agreement with the experimental value.

We can calculate the strain energies for the six-membered ring using the following reactions (thermochemical data from ref 6):

$$C_5H_{10}S(g) + 4C_2H_6 \rightarrow CH_3CH_2SCH_2CH_3 + 3CH_3CH_2CH_3 \quad (16)$$

$$\Delta H_r(16) = 1.1 \text{ kJ mol}^{-1}$$

$$C_5H_{10}SO(g) + 4C_2H_6 \rightarrow CH_3CH_2SOCH_2CH_3 + 3CH_3CH_2CH_3 \quad (17)$$

$$\Delta H_r(17) = -9.9 \text{ kJ mol}^{-1}$$

$$C_5H_{10}SO_2(g) + 4C_2H_6 \rightarrow CH_3CH_2SO_2CH_2CH_3 + 3CH_3CH_2CH_3 \quad (18)$$

$$\Delta H_r(18) = -13.4 \text{ kJ mol}^{-1}$$

Thiane does not appear to be strained, whereas the strain energies of the sulfoxide and sulfone are similar in magnitude and differ by approximately the free energy difference suggested for equatorially substituted thiane 1-oxide. Given the similarities in geometry, these enthalpic differences could reflect the presence of the equatorial oxygen in the sulfone.

Conclusions

Calorimetric measurements on crystalline **4** afforded accurate values for its enthalpies of combustion and sublimation. The derived thermodynamic parameter for the standard molar enthalpy of formation in the gas

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[55] Experimental $\Delta_f H°_m$ values for the reference compounds used in isodesmic reactions 10−13, methane, ethane, propane, cyclohexane, dimethyl sulfoxide, and dimethyl sulfone, −74.9, −83.8, −104.7, −123.0, −150.5, and −373.0 kJ mol^{-1}, respectively, have been taken from a NIST compilation: Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. Neutral Thermochemical Data. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, July 2001 (http://webbook.nist.gov).

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[57] Experimental $\Delta_f H°_m$ values for thiane and atomic oxygen, −63.5 and 249.18 kJ mol^{-1}, respectively, have been taken from a NIST compilation. See ref 55.

TABLE 6. Enthalpies of Formation of Thiacyclohexane 1-Oxide and Thiacyclohexane 1,1-Dioxide, Experimental and Calculated from Atomization, Isodesmic, and Bond Dissociation Reactions[a]

	G2(MP2)			G2(MP2)+			
compd	atomization	isodesmic	bond dissociation	atomization	isodesmic	bond dissociation	exptl
5	−176.3 (−182.9)[b]	−179.3,[c] −180.7[d]	−177.7,[e] −180.4[f]	−174.1 (−180.7)[b]	−178.7,[c] −180.5[d]	−178.0,[e] −177.8[f]	(−174.0)[g]
4	−391.2 (−401.4)[b]	−402.0,[h] −403.2[i]	−392.0[j]	−391.7 (−401.9)[b]	−401.2,[h] −402.9[i]	−395.0[j]	−394.8 ± 1.4

[a] All values in kilojoules per mole. [b] Value obtained from atomization reaction including spin−orbit and bond additivity corrections. See the text. [c] Value obtained using isodesmic reaction 10. [d] Value obtained using isodesmic reaction 11. [e] Value obtained using bond dissociation reaction 14. [f] Value obtained using bond dissociation reaction 1. [g] Value obtained through bond dissociation reaction 1, using the experimental S═O bond dissociation energy in sulfones, taken from ref 10. [h] Value obtained using isodesmic reaction 12. [i] Value obtained using isodesmic reaction 13. [j] Value obtained using bond dissociation reaction 15.

phase, $\Delta_f H°_m(\mathbf{4},g) = -394.8 \pm 1.5$ kJ mol^{-1}, is very negative when compared with the reported enthalpy of formation of the thioether analogue **3**, $\Delta_f H°_m(\mathbf{3},g) = -63.5 \pm 1.0$ kJ mol^{-1}.[6] This huge enthalpic difference, $\Delta\Delta_f H°_m(\mathbf{4}-\mathbf{3}) = -331.3$ kJ mol^{-1}, is a manifestation of the remarkable strength of the S═O bonds, as well as the significantly stronger C−SO$_2$ bonds in **4**.

With the value of the enthalpy of formation of **4** at hand, and given the known enthalpy of formation of atomic oxygen in the gas phase, $\Delta_f H°_m(O,g) = +249.18$ kJ mol^{-1},[11] as well as the reported bond dissociation energy for the S═O bond in alkyl sulfones,[10] BDE(S═O) = +470.0 kJ mol^{-1}, it was possible to estimate the enthalpy of formation of **5**, a hygroscopic compound difficult to use in experimental calorimetric measurements, $\Delta_f H°_m(\mathbf{5}) = -174.0$ kJ mol^{-1}.

The molecular structures of **4** and **5** were optimized at the MP2(FULL)/6-31G(3df,2p) level of theory, and showed excellent agreement with the experimentally obtained geometrical parameters.[21,22] It was found that (at the MP2(FULL)/6-31G(d) level) the conformational isomer with the oxygen atom in the axial position for **5** is 7.4 kJ mol^{-1} more stable than the conformer with an equatorial sulfinyl S═O group. This calculation is also in agreement with experiment.[26c]

The enthalpies of formation of both **4** and **5** that are experimentally determined in this work were closely reproduced by theoretical calculations, at the G2(MP2)+ level.

Finally calculated G2(MP2)+ values for the bond dissociation energy of the S═O bond in cyclic sulfoxide **5** and sulfone **4** are 363.7 and 466.2 kJ mol^{-1}, respectively.

Experimental Section

Materials. Thiacyclohexane 1,1-dioxide was synthesized following the method described in ref 58. ^{1}H NMR, ^{13}C NMR, IR, and Raman spectra are given as Supporting Information. The compound was purified by crystallization from hexane−methylene chloride. Control of purity assessed by DSC using the fractional fusion[59] technique indicated that the mole fraction of impurities was less than 0.0004. The DSC curve is given in the Supporting Information.

The sample was studied by DSC over the temperature range 273−378 K, and no solid−solid phase transition was found.

Procedure for Thermochemical Measurements. An isoperibol calorimeter equipped with a rotary bomb and an isothermal jacket was used for the measurements of the energy of combustion. The apparatus and procedure have been described in ref 1. To confirm the chemistry of the combustion process and the accuracy of the energy correction involved in the analysis of results, thiantrene was used as the reference material.[60] The standard molar enthalpy obtained, $\Delta_c H°_m = -7242.1 \pm 3.0$ kJ mol^{-1}, is in good agreement with the values obtained by other authors.[60] All the details of the combustion measurements and the physical properties used for the determination of the energy of combustion are given as Supporting Information.

A differential scanning calorimeter equipped with an intracooler unit was used in this research to measure the heat capacities of the compound, to control the purity, and to study the phase transitions of the sample. Heat capacities were determined following the method described in ref 61. Synthetic sapphire and benzoic acid were used as reference materials[60] for checking all the process.

The vapor pressures as a function of the temperature of thiacyclohexane 1,1-dioxide were determined by the mass-loss Knudsen-effusion method using the tested technique and procedure previously described (benzoic acid and naphthalene as reference materials).[62] The enthalpy of sublimation was deduced from the temperature dependence of the vapor pressures.

The Clausius−Clapeyron equation

$$\ln (p/p°) = -B\,T^{-1} + A \qquad (19)$$

where $p° = 101.325$ kPa, was fitted to the vapor pressures to give the molar enthalpy of sublimation from $B = \Delta_{sub}H°_m\langle T_m\rangle/R$, where $R = 8.3145$ J K^{-1} mol^{-1}. The uncertainties assigned to the value of the enthalpy of sublimation are the standard deviation of the B value.

Full experimental details are given as Supporting Information.

Computational Details. Standard ab initio molecular orbital calculations[54] were performed with the Gaussian98 series of programs.[63] The energies of the compounds studied were calculated using Gaussian-2 theory, at the G2(MP2)[49] level.

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G2(MP2) corresponds effectively to calculations at the QCISD(T)/6-311+G(3df,2p) level on MP2(full)/6-31G(d)-optimized geometries, incorporating scaled HF/6-31G(d) zero-point vibrational energies and a so-called higher level correction to accommodate remaining deficiencies.

We have also reoptimized the geometries at the MP2(full)/6-31G(3df,2p) level to obtain more reliable molecular structures for the compounds studied.

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Supporting Information Available: Experimental details, tables of results for the determination of $\Delta_f H^\circ_m$, IR, Raman, ^{1}H NMR, and ^{13}C NMR spectra and DSC curve of purity control for thiacyclohexane 1,1-dioxide, and tables with experimental and calculated frequencies and Cartesian coordinates of thiacyclohexane 1-oxide and thiacyclohexane 1,1-dioxide. This material is available free of charge via Internet at http://pubs.acs.org.

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